

A STUDY OF LOW DENSITY, HIGH STRENGTH  
HIGH MODULUS COMPOSITES

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## ABSTRACT

This is the second quarterly report on contract NAS W 1020. It is concerned with composites for space vehicle structural applications. During this quarter, work has been concerned with a filament winder to produce metal matrix composites, filling sapphire whisker mats with nickel, investigating nickel and aluminum overcoats on boron filaments, and the investigation of the vapor deposition of  $\text{Al}_2\text{O}_3$ . Preliminary composites have been made during operational check-out of the winding machine and a cross section photograph is shown. Sapphire wool mats from Thermokinetics, Inc., have been filled with a nickel matrix. A cross section photograph is shown and no voids are apparent. Both nickel and aluminum have been applied as overcoats to boron filaments and cross section photographs are shown. Preliminary studies were conducted to vapor deposit  $\text{Al}_2\text{O}_3$  to subsequently produce  $\text{Cb-Al}_2\text{O}_3$  composites. Initial deposition runs produced good deposits of  $\text{Al}_2\text{O}_3$ .

## I. INTRODUCTION

This is the second quarterly progress report on contract NAS W 1020. It is an informal report submitted in response to Article V, Section a, Progress Reports, of the subject contract.

Many reports have been compiled by individuals and committees on the requirements and recommendations of materials research for missile and space applications. The temperature environments range from cryogenic to ultra-high re-entry conditions and pressure environments from atmospheric to hard vacuum. Across this spectrum there are several common properties that a material should possess to be useful in space vehicles. These are low density, high modulus, and high strength. If a material has at least two of these properties, then it can be used in high performance applications. The specific configuration of the reinforcement is dictated by the mission.

There are several materials which are outstanding for low density, high modulus, and strength. These materials are beryllium, boron, and the carbides, borides, nitrides, and silicides of metals with an atomic number less than about 22. Except beryllium, these materials are rarely used in bulk form because of the high modulus property. They are more efficiently utilized in very fine filament and ribbon form interdispersed in a matrix. It will be through the development of such unique composites that major materials advancement will be made. The specific geometric form (circular cross-section, ribbon, etc.) of the reinforcement material and the matrix in which it is interdispersed depends on the application.

The objective of the subject contract is the exploratory investigation of generalized classes of composite materials. These classes of composites are believed to possess properties advantageous for applications involving extreme environments for space vehicle structural applications. Since the reinforcement materials to produce advanced composites are unusual and

are not commercially available, it is necessary first to produce them in order to fabricate a composite and measure its properties. Initially the experimental investigations are mainly concerned with investigating and producing the reinforcement materials.

The composite materials which are being investigated in this generalized study consist of matrices of metals and ceramics and reinforcements in the form of particle, flake, and filament. Metal matrices are being emphasized and, in keeping with the low density requirement, only metals with an atomic number less than 28 are being investigated. The reinforcement phases being investigated are the general class of high modulus materials with emphasis on the materials beryllium, boron, silicon carbide, and boron carbide in the form of filaments and flakes. The filaments will be in various cross-sections such as round and flat ribbons.

Some other specific composite materials are being investigated. These are multi-layer metal-ceramic composites formed by building up successive alternate layers of a metal followed by a ceramic until a billet-type material has been built up. Although glass filaments do not have a high modulus, a composite of glass-reinforced aluminum will result in a composite with a very high strength-to-weight ratio. The strength-to-weight ratio is especially important in space vehicle structures and values of 2,000,000 are regularly obtained using glass-reinforced plastics. However, plastic matrix composites are restricted to below 600° F., and they are inferior to metals at cryogenic temperatures. A high silica glass-reinforced aluminum composite has the potential of exceeding the strength-to-density ratio of glass-plastics composites and has the added advantages of operating to temperatures of 1200° F. with improved properties at cryogenic temperatures.

This investigation will demonstrate that significant advancements in composites for space vehicle structural applications can be achieved through the investigation and production of unique and unusual reinforcement and matrix combinations.

## II. RESULTS

During the second quarter, the following areas have been investigated: (1) a filament winder to produce a metal matrix composite while winding a filament on a mandrel, (2) multi-layer composite filaments, and (3) depositing multi-layer metal-ceramic composites.

### A. FILAMENT WINDER AND METAL MATRIX COMPOSITES

The General Technologies Corporation had developed previous to this contract a technique of simultaneously winding a filament on a mandrel and depositing a metal matrix to result in a composite not requiring further consolidation. We intend to use this technique to produce composites with the various reinforcements that are produced.

In our initial efforts, hand winding of tungsten wire and glass filaments as reinforcements was used. Nickel deposition during winding resulted in a nickel matrix with tungsten wire or glass filament reinforcements. Composites of varying volume per cent filler were produced to demonstrate the feasibility. These studies showed that to produce composites utilizing varying size and shape reinforcements and to produce composites with varying volume per cent filler, an unusual winding machine would be required. No commercially available machine would meet the requirements of having a traverse variable from 0 to over one foot, provide variable tension on the winding filament, accommodate filament sizes of 0.5 mils to 10 mils, and wind the filaments with variable spacings without overlap and to a tolerance of  $\pm 1$  mil. The most adaptable piece of equipment to build a winder to meet these requirements was a lathe. A 12 inch lathe was used and modified to meet the winding requirements given above. Considerable time during this latter quarter has been devoted to modifying the lathe to utilize it as a winding machine. A photograph of it is shown in Figure 1.

We have just begun to make windings on this machine, and Figure 2 shows a cross-section

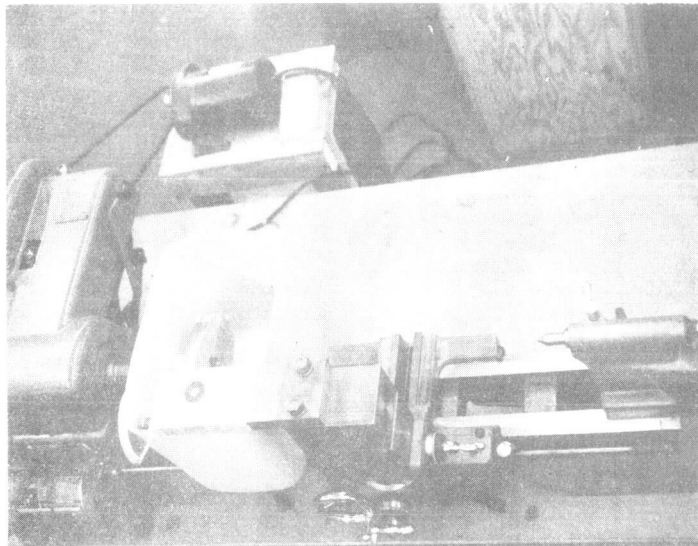
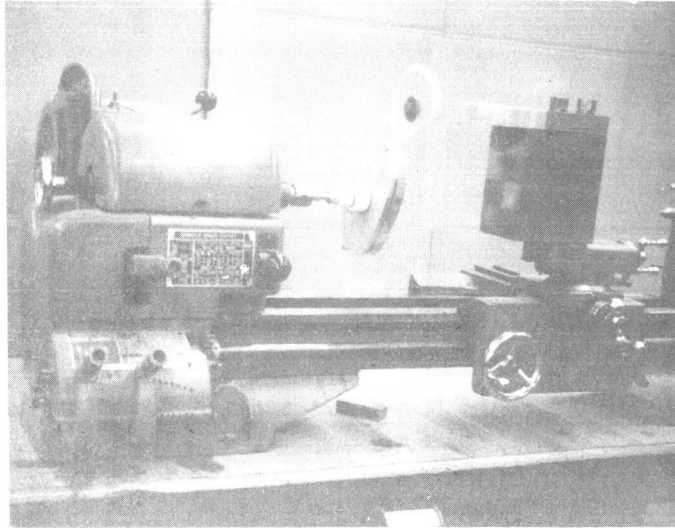


Figure 1. Two views of a lathe modified for filament winding to produce metal matrix composites.

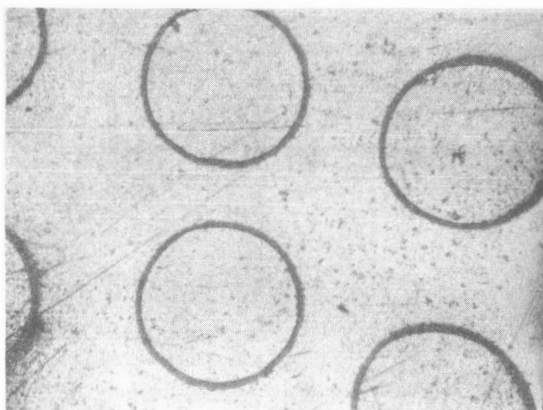


Figure 2. Composite of copper transformer wire-nickel matrix made in demonstrating operability of winding machine in Figure 4. 180X

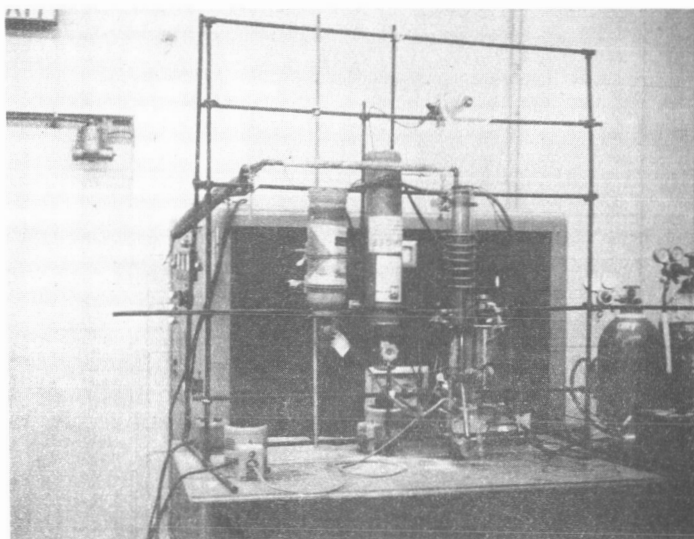


Figure 4. Vapor deposition set-up showing induction heating.

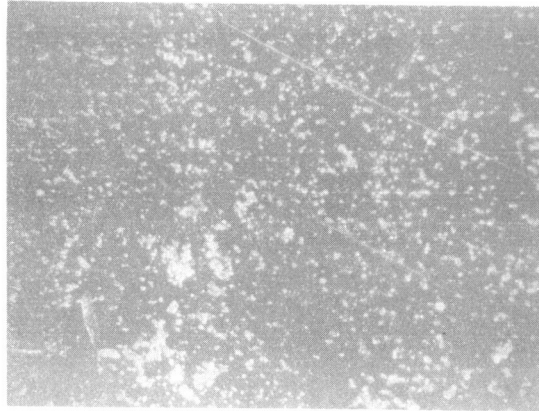
of a composite formed in demonstrating the operation and potential of this machine. In the future, composites will be made and physical property data determined.

### 1. Metal Matrix Whisker Composites

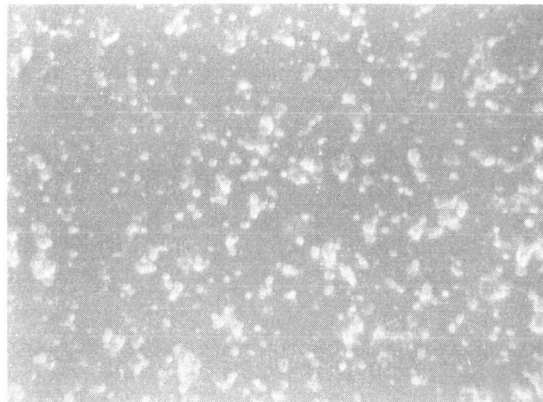
The unusual high physical properties of whisker materials make them very attractive as reinforcing agents in metal matrices. As an example, sapphire whiskers are commercially available, having tensile strengths of  $2-3 \times 10^6$  psi and elastic modulus of  $100-300 \times 10^6$  psi at room temperature. The retention of these properties at elevated temperatures are unusually good. If a metal matrix composite can be produced utilizing whiskers with any degree of efficiency, a very effective engineering material will result. Metal matrix composites utilizing sapphire whiskers have been made using casting and liquid metal infiltration techniques. These techniques are restricted to low melting matrix materials and frequently the molten metal degrades the whiskers. For an effective engineering material, matrices of aluminum, titanium, chromium, and nickel should be used. The high melting point of all these except aluminum restricts their use by the previous forming methods.

We have utilized a previously developed deposition technique to fill mats of sapphire whiskers. Figure 3 shows a nickel-filled mat of sapphire whiskers. The composite consists of about 3 volume per cent of 3-9 micron randomly-oriented sapphire whiskers and 97 volume per cent nickel. The composite was formed at room temperature without damage to the whiskers and is without voids. It is planned to do more work in this area and obtain some physical property data on the composites produced. Ultimately, it is planned to produce fiber reinforced metal matrix composites with whiskers interdispersed. Such a material would have high tensile and compressive strengths due to the fibers and high shear strengths due to the whiskers. Both the fibers and the whiskers would contribute to high modulus.





Nickel Matrix Sapphire Wool Composite  
Made by Deposition of the Nickel to Fill  
in the Wool Mat. 400X



Nickel Matrix Sapphire Wool Composite  
Made by Deposition of the Nickel to Fill  
in the Wool Mat. 800X

Figure 3.

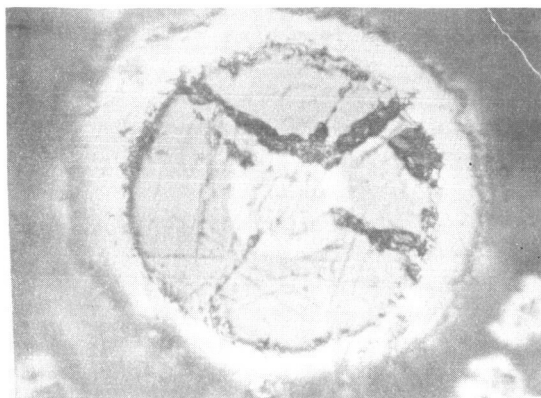
## B. PRODUCTION OF REINFORCEMENTS

The reinforcing materials which meet the requirement of low density, high strength, and high modulus are not commercially available and must be fabricated in order to investigate advanced space vehicle structures. The form of reinforcing agents used depends on the properties desired in the composite. Since this is a general study, we intend to investigate reinforcements in the form of circular filaments, flat ribbons, flakes, and, in some cases, particles. Most of the past work has been concerned with circular cross sections.

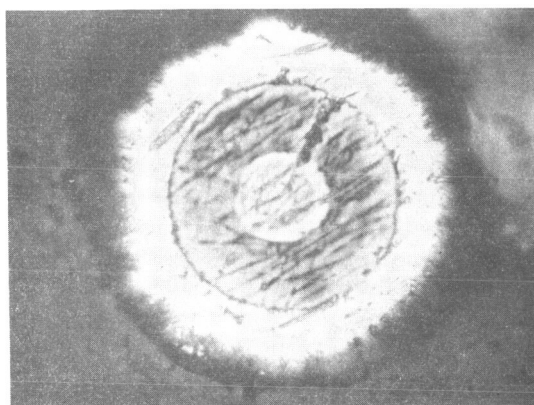
During the first quarter, filaments of boron, boron carbide, and silicon carbide were fabricated. The reaction routes to produce these filaments were the  $H_2$  reduction of  $BCl_3$ , the  $H_2$  reduction of  $BCl_3$  in an atmosphere of toluene, and the  $H_2$  reduction of  $HSiCl_3$  in toluene. The physical properties of these filaments were reported in the first quarterly report.

The boron filaments have been used as a base to form multi-layer filaments as suggested by the NASA Headquarters Project Managers. The multi-layer filaments are being investigated to determine the effect of a low modulus ductile material as an overlay on a high modulus filament. Such a coating could aid in handling the high modulus filaments and prevent damage, serve as a matrix to form a composite by fusing the bundles together, and serve as a wetting and load transmitting layer between matrix and filament as well as other possible applications. Aluminum and nickel have been selected as the overlay metal coating.

The apparatus used to vapor deposit the nickel and aluminum on the boron filament is shown in Figure 4. A few coatings have been made on the boron filaments, and a cross-section is shown in Figure 5. The cracks in the boron filaments are due to mounting and polishing. The nickel and aluminum are on the same boron filament, and only one crack is in the aluminum-coated filament. The fact that cracks are due to mounting and polishing is evidenced by the fact that a given filament can be polished and show cracks, then further polished and



Nickel on boron filament - Boron by  $\text{BCl}_3$  and nickel from carbonyl. 500X



Aluminum on boron filament - Boron by  $\text{BCl}_3$  and aluminum from isobutyl. 400X

show less or more cracks in different positions, and, in some cases, no cracks at all are observed.

Additional filaments will be coated and characterized in the monofilament form and they utilized in composites and compared to composites without the ductile metal coating.

### C. MULTI-LAYER CERAMIC-METAL COMPOSITES

In work conducted by Professor F. R. Shanley of U.C. L.A., it has been shown that multi-layer metal-ceramic composites have very high potential in structural and high temperature applications. In Shanley's work, alternate layers of metal and ceramic were built up by plasma or flame spraying. Each layer was a few mils thick. After the layers had been built up many layers thick, the "billet" was powdered and reconstituted into a cermet which had unusual ductility and high temperature resistance. The ductility was attributed to the many metal-ceramic interfaces (slip planes) within each particle making up the cermet. These slip planes are randomly oriented throughout the cermet. Such a material has high potential as structural material involving high temperature use. In addition to the use of the multi-layer ceramic-metal material for reconstitution into a cermet, it has potential as a prestressed structural material.

The main deterrent to investigating this class of materials lies in the lack of a practical procedure for fabricating them. Metal spraying is difficult to control in depositing thin layers of metals and ceramics. The ultimate potential in this class of materials can only be realized in depositing controlled thin layers of the metals and ceramics - as an example, thickness desired range in the vicinity of 0.2 mils for the metal layers and 1.0 mils for the ceramic layers. Chemical vapor deposition is a process which can be used to control deposit thin films of metals and ceramics. Since we have an excellent capability to vapor deposit both ceramics and metals, we felt it worthwhile to investigate the unusual and high potential class of composite materials.

To avoid building in stresses between the metal and ceramic due to thermal expansion differences, we feel that as close a match in expansion as possible should be attained. An almost ideal match in expansions is between columbium and  $\text{Al}_2\text{O}_3$ . This will be the initial system investigated; however, other ceramic-metal combinations in which metals having a somewhat higher and lower expansion than the selected ceramic will be investigated.

We have vapor deposited columbium in the past with no difficulty by the reduction of  $\text{CbCl}_5$ . We feel there is no problem in depositing this metal, and it has not been investigated during this quarter. In the case of the ceramic material, we have deposited thin films of  $\text{Al}_2\text{O}_3$  in the past by the water-gas reaction. Although good deposits are obtained, the rate is reasonably slow (about 1 mil/hr.) and we felt other deposition processes offer equal or better potential. The thermal decomposition of aluminum isopropyl oxide was investigated. Although the process has not been completely worked out, deposition at the rate of 10 mils/hr. was obtained. The deposits were extremely smooth and fine grained. It is felt this deposition system is superior to the water-gas reaction, and it will be further investigated to produce multi-layer Cb- $\text{Al}_2\text{O}_3$  composites. Composites of about 80%  $\text{Al}_2\text{O}_3$ -20% Cb will be made and investigated in sheet form under prestressed conditions, and reconstituted cermets made. The cermets will be characterized with respect to density, compressive strength, tensile strength, and ductility.

### III. WORK PLANNED FOR NEXT QUARTER

1. Wind metal matrix composites and test.
2. Produce additional filaments and apply an overcoat of nickel or aluminum and characterized in monofilament form and in composites.
3. Complete deposition studies on the deposition of  $\text{Al}_2\text{O}_3$  and make some composites of  $\text{Al}_2\text{O}_3$ -Cb.